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Conf-9007117--4

UCRL-JC--105105

DE91 012081

MAY 21 1991

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**This paper was prepared for submittal to SPIE Conference
San Diego, CA
July 1990**

October 18, 1990

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Radio frequency and microwave plasma for optical thin film deposition*

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1. Introduction

For the next generation of fusion lasers reflecting mirrors with laser damage thresholds of at least 40 J/cm^2 for 10 ns laser pulses at $1.064 \mu\text{m}$ are needed. Up to now, no deposition technique has been developed to produce such mirrors. Best R&D-values realized today are around 30 J/cm^2 for e-beam evaporated mirrors. R&D on conventional e-beam coating processes over the last 10 years, has come up with marginal improvements in laser damage thresholds only. However, new technologies, like PICVD (Plasma-Impulse CVD) developed for the fabrication of ultra-low loss fiber preforms, seem to offer the potential to solve this problem. First results have been reported already [1-3]. It is well known that fused silica produced by CVD processes can have laser damage thresholds as high as 80 J/cm^2 . However, the thickness of a single deposited film is in the μm -range for most of the CVD-processes used for preform manufacturing; since interference optics need films in the $\lambda/4n$ range (where n is the refractive index of the dielectric material) the use of preform-fabrication processes for the purpose of interference mirror fabrication is limited to a few plasma based CVD technologies, namely PCVD (Plasma-CVD, Phillips [4]; PICVD, SCHOTT [5]). Especially PICVD is a very powerful technology to fabricate thin film multilayers for interference mirrors, because this technique is able to produce films down to monolayer thickness with nearly perfect stoichiometry and morphology. In first and preliminary experiments the usual deposition in a circular tube at high temperatures has been used for simplicity. However, to produce large area high quality laser mirrors this principle know-how has to be transferred from circular to planar geometry. Experiments showed, that there may be some limitations with respect to the homogeneity of a planar deposition using microwave excitation for the plasma. Therefore experiments have been performed in parallel with both RF and microwave excitation for comparison. In the following we will restrict ourselves to the description and discussions of the planar processes; the principle and details of the PICVD-process are described elsewhere [5] while RF-plasma technology is a well known process.

2. Multilayers

A multilayer can be prepared by a CVD-process by periodically mixing SiO_2 precursor gas flow with dopant precursor gas flows. This leads to a periodical doping of the growing SiO_2 layer. Thermal mismatch of pure and doped SiO_2 limits the refractive index difference which can be produced by

*This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

the doping. High reflectance can nevertheless be achieved by fabrication of a large number of layer pairs. This also meets the consideration that multilayers for high power lasers should be constructed such as to avoid strong field enhancements at the boundary of high and low refractive index layers, i. e. small index difference as well as very small index gradient should be used. Therefore a sinusoidal refractive index profile should be preferred [6].

Fig. 1: Reflection curve of a 500 periods filter with rectangular refractive index change and $\delta n = 0.02$

Fig. 2: Reflection curve of 500 periods filter with triangular refractive index change and $\delta n = 0.02$

2.1 Theoretical calculations

Reflection spectra of low refractive index difference filters (LRIDF) have been calculated for various shapes of refractive index profiles and - for simplicity - for a peak wavelength of $1 \mu\text{m}$. Rectangular and triangular profiles (Figs. 1, 2) do not show the first but the second harmonic only. A pure sinusoidal LRIDF, a so called Rugate-filter [6], however, has no harmonics, if the refractive index difference is small compared to the period number (Fig. 3); if not, the first harmonic appears at $\lambda_0/2$ (Fig. 4). Harmonics at $\lambda_0/2$ result also from disturbed (change in period) sinus profiles (Figs. 5 a,b).

In all cases the reflection is very high.

Fig. 3: Reflection curve of a 500 periods filter with sinusoidal refractive index change and $\delta n = 0.02$

Fig. 4: Reflection curve of a 100 periods filter with sinusoidal refractive index change and $\delta n = 0.1$

Fig. 5: Same as Fig. 3 but disturbances of 10 % (a) or 20 % (b) of the period length

2.2 General practical aspects of mirror preparation

Conventional mass flow controllers used for the experiments described here are not at all able to form doping-gas mass flows having the same waveform as the corresponding set points. A square waveform setpoint forms a mass flow with a smooth rise and a steep descent. The peaks of a mass flow formed by a triangle waveform are rounded and the mass flow formed by a sinusoidal waveform is (slightly) deformed too.

Fig. 6: Reflection curve of an experimental filter consisting of a stack of three different filters with rectangular, triangular, and sinusoidal refractive index change, respectively; each filter has 100 periods and $\delta n = 0.025$

Fig. 6 shows the transmission spectra of a stack of 3 filters, each consisting of 100 periods ($\delta n = 0.025$) with refractive index modulations differing in period and form. The main peak comes from the sinusoidal form; the triangle and square main peaks are at wavelengths longer than 1200 nm. Each waveform type produces harmonics of several orders which are caused - to some extent - by deviations from the setpoint mass flows.

3. The RF-Planar CVD-System

3.1 Experiments

Preliminary deposition studies were carried out in a horizontal silica tube reactor, shown schematically in Fig. 7. The tube was 7.62 cm in diameter (expanded to 12 cm in the reaction zone) and approximately 61 cm long. The tube was contained in a radiantly heated furnace with the heating zone approximately 30 cm long. A thimble containing a fused silica substrate on a graphite plate

Fig. 7: Schematic of radiantly heated RF-plasma CVD reactor

served as the absorber in the radiant furnace and as the driving electrode for the application of RF at 13.56 MHz. Gas flows of O_2 , $SiCl_4$ and $GeCl_4$ were established using mass flow controllers. Pressures were monitored with Baratron gauges and controlled by a butterfly valve controller. Typical operating parameter ranges are given in Table 1.

3.2 Preliminary Deposition Experiments

Preliminary deposition experiments using 13.56 MHz RF to drive the reactive plasma in the horizontal, radiantly heated furnace pointed out several significant problem areas. First, the substrate temperature was difficult to determine. The thermocouple monitor could only read the back of the susceptor and was influenced by the driving RF electric field. Second, the deposited layers were uneven and contained particulates. The existence of cold walls in contact with the process caused generation of a silica particles, which found its way onto the growing film. Also, there was considerable leakage of the plasma into undesirable areas of the reactor, such as directly behind the susceptor and along the walls of the thimble. This leakage significantly reduced the plasma power density available in the reaction volume. In addition, the total RF power available was only 1 kW.

Table 1: Summary of typical operating conditions used in our preliminary radiant heating RF-plasma CVD experiments

Pressure	0.3-3.0 torr
Flow rate oxygen	100-500 sccm
Flow rate SiCl_4	20-90 sccm
Flow rate GeCl_4	0-10 sccm
RF power (CW exp.)	300 Watts
RF power (peak)	57-94 Watts
RF power (average)	8.5-15 Watts
Pulse width	$10-15 \cdot 10^{-3}$ s
Pulse Repetition Frequency	10-30 Hz
Temperature	1050-1250°C
Reaction time	60 min
Number of experimental runs	16

3.3 Hardware Development

Based on the results of the preliminary investigations, a coating system was specified by LLNL and designed and built by Prototech Research Inc. A schematic of the coating chamber is shown in Fig. 8. It is capable of handling fused silica substrates up to 15 cm in diameter and 1 cm thick. The furnace is a 3-zone back-heating system designed to heat the substrates to about 1000°C. Some details regarding the reaction environment are described in Table 2.

Table 2: Summary of designed operating characteristics of the high temperature, RF-plasma CVD coating system

Substrate Size	15 cm dia. x 1 cm thick
Oxygen Flow Rate	0-8 sccm
SiCl_4 Flow Rate	0-2 sccm
GeCl_4 Flow Rate	0-500 sccm
RF Power	24 kW maximum
Substrate Temperature	1000°C nominal, 1200°C max.

Fig. 8: Schematic drawing of the RF-PCVD coater reaction chamber

The "hot wall" reactor is formed by using closed-cell porous silica glass to enclose the reaction volume and absorb radiant energy from the furnace. Gas is injected through a top plate via an array of gas injection ports and exhausted out the top at the periphery of the substrate. The containment vessel for the furnace acts as an electrode for a 24 kW 13.56 MHz RF-generator. Plasma confinement is achieved by isolating the walls of the electrode with a silica thimble which is evacuated to less than 10^{-4} torr. The absorbing silica provides dielectric insulation to suppress plasma breakdown outside of the reaction chamber. The coating apparatus is located in a clean box to prevent particulate contamination. This coater is designed to be as flexible as possible to allow for design changes to meet coating process demands.

4. The Microwave Plasma Planar CVD-System

4.1 Status of achieved results

Multilayer systems designed for high reflectance at 1064 nm were prepared at the inner surface of quartzglass tubes [1,7]. Typical deposition parameters are given in Table 3. Enhancing the substrate temperature increases the diffusivity and decreases the incorporation efficiency of fluorine into the SiO_2 network. Because the geometrical distance between a maximally F-doped and an

Table 3: Typical deposition parameters for high temperature microwave PICVD

tube type	Heralux WG
tube size	20 mm x 1.4 mm
tube temperature	850°C
pressure	3 mbar
oxygen-mass flow	200 ml/min
SiCl ₄ -mass flow	50 "
CCl ₂ F ₂ -mass flow	10 " , maximal
modulation	sinusoidally
period time	0.9 s
No. of periods	500

undoped SiO₂ layer is 181 nm only, the substrate temperature should be as low as possible in order to prevent a smoothening of the refractive index difference by diffusion. On the other hand the lower temperature limit is given by the temperature for low stress deposition. These aspects lead to a substrate temperature of 850°C.

Fig. 9 shows a segment of a broken quartzglass substrate with a deposited multilayer system. There is no boundary visible between substrate and coating, demonstrating the glassy structure of the coating. Wet etching of such samples with a HF containing solution transforms the periodical index difference to a periodical surface profile due to the dopant content dependence of the etching rate. A SEM picture of a section of a 500 period system is displayed in Fig. 10. The distance from layer to layer (i. e. in the SEM picture from the black/white to the white/black interface and vice versa) is 181 nm corresponding to $1064 \text{ nm}/4n$. No defects or deviations can be seen in the array. Laser damage thresholds measured at Lawrence Livermore National Laboratory with 10 ns laser pulses at 1064 nm exceed 40 J/cm^2 for both F- and Ge-doped multilayer systems; however, because of the curved substrates these measurements were quite difficult to perform and the results are estimated to be pessimistic values.

4.3. Planar depositions

A Rugate filter with a small δn (< 0.02) has a very narrow reflection peak of typically 10 nm half-width at 1064 nm. So the uniformity of the deposition rate across the substrate should be at least 1 % so that the reflections peak coincides with the laser wavelength all over the substrate area. Because of the essential importance of the film uniformity, the development of the planar micro-

wave coater is done in two steps. At first the coater design and the operation parameters are optimized empirically by using a setup made for room temperature depositions. On the basis of these experiences the concept for a high temperature coater has been developed, which is being built at present at SCHOTT.

Fig. 9: Broken substrate tube with deposited multilayer system

Fig. 10: SEM-picture of an etched multilayer (line corresponds to $1 \mu\text{m}$)

The experimental arrangement of the room temperature coater is shown in Fig. 11. The substrate is placed on a base plate (glass) below a gas distributor inside a glass bell jar, through which the exhaust gas is pumped off. The gas distributor consists of a 5 mm thick aluminum plate with holes of 1.2 mm diameter drilled into it every 5 mm and a gas plenum above it. The reaction gas is fed into the gas plenum via a small tube with 13 holes at the end, which provide a uniform distribution of the gas over the 450 distributor holes. The microwave power is applied by an antenna below the base plate. The whole apparatus is surrounded by a shielding cage to avoid any leakage of the microwave. The metallic gas distributor plate acts as an upper confinement for the propagation of microwave. With proper tuning it is possible to ignite a stable plasma of 120 mm diameter right above the substrate with a pulse power of 3-4 kW (in 1 mbar O_2 plus 1 % TiCl_4).

The film uniformity can easily be estimated from the colours of the interference patterns of a TiO_2 film deposited from a TiCl_4 plasma due to the high refractive index of TiO_2 . Quantitative values of

Fig. 11: Schematic drawing of the microwave PICVD reaction chamber for room temperature experiments

Fig. 12: Thickness homogeneity of a PICVD-deposited TiO₂-film measured across the substrate

Fig. 13: Deposition rate versus pressure for TiO₂-deposition at room temperature

the film thickness are obtained by covering a stripe of the substrate during deposition and measuring the height of the edge with an Alpha step 200 film profile (Tencor Instruments). A typical result of a thickness measurement across the substrate is shown in Fig. 12. The film thickness is rotationally symmetric in most cases. With optimal parameters, listed in Table 4, the maximum devi-

ation of the thickness from the average value is $\pm 3\%$ at this state of development. The possibility to improve the uniformity by mechanical movement of the substrate was not considered.

The deposition rate varies linearly with pressure as shown in Fig. 13. In this experiment the mass flow was increased proportional to the pressure in order to keep the gas velocity constant and thus not alter the gas exchange in the reactor. The deposition rate will be 20 times higher for SiO_2 deposited at high temperature due to a larger amount of source chemical (20 % SiCl_4 in O_2) possible in the high temperature process and will typically reach 1-2 $\mu\text{m}/\text{min}$.

Table 4: Typical parameters for TiO_2 microwave-PICVD deposition at room temperature

substrate diameter	120 mm
pressure	0.7 mbar
oxygen-mass flow	100 ml/min
TiCl_4 -mass flow	1.0 ml/min
pulse power	4.0 kW
pulse duration	0.8 ms
pulse pause	90 ms
average power	35 Watts
deposition rate	33 nm/min
uniformity of thickness	$\pm 3\%$
refractive index of TiO_2	2.5 (at 500 nm)

4.4 Conclusions

The PICVD process is well suited for the preparation of multilayers. Important features are:

- a quarterwave layer is composed of many monolayers in the nanometer range;
- both high deposition rate and arbitrary refractive index profiles are feasible simultaneously;
- low refractive index difference and a high number of layer pairs can be realized;
- multilayer thickness can amount to the mm range;
- laser damage thresholds are very high.

5. Conclusions

We have recently shown that very high damage threshold dielectric coatings can be made using plasma CVD at high temperatures (1000°C) [1]. In this paper we discussed our efforts at scaling this process to larger, flat substrates (10 cm diameter) as well as comparing RF and microwave plasmas. There are four main technical issues that must be solved to successfully implement this

coating process:

1. Uniform deposition ($\pm 1-5\%$) over a large area
2. High deposition rates ($1-4\ \mu\text{m}/\text{min}$)
3. Uniform substrate heating of temperatures up to about 1000°C
4. Minimal dopant diffusion

In addition, work is in progress to look at the effects of RF versus microwave driven plasma on the deposition process and we have begun to identify and refine plasma characterization techniques. Based on these results we have built a large coating system designed to coat substrates up to about 15 cm in diameter with several thousand quarter-wave layers of alternating doped and undoped SiO_2 . Details of the coater design specifications have been formulated and given. The system is expected to be fully operational by mid-1990.

6. Acknowledgement

We would like to thank Dr. U. Fotheringham for the theoretical calculations, Mr. Messinger for optical measurements as well as Mrs. Blecker and Mrs. Blenefeld for the PICVD-experiments.

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